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Intra- and inter-chain fluctuations in entangled polymer melts in bulk and confined to pore channels

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Abstract

It is known that topological restraints by "chain entanglements" severely affect chain dynamics in polymer melts. In this field-cycling NMR relaxometry and fringe-field NMR diffusometry study, melts of linear polymers in bulk and confined to pores in a solid matrix are compared. The diameter of the pore channels was 10 nm. It is shown that the dynamics of chains in bulk dramatically deviate from those observed under pore constraints. In the latter case, one of the most indicative signatures of the reptation model is verified 28 years after its prediction by de Gennes: The frequency and molecular mass dependencies of the spin-lattice relaxation time obey the power law $T_1 \propto M^{3/4}$ on a time scale shorter than the longest Rouse relaxation time τ_R . The mean squared segment displacement in the pores was also found to be compatible to the reptation law $\propto M^{-1/2}t^{1/2}$ predicted for τ_R